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## Topological Effect on Polymer Crystallization of Linear and Ring Polymers

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### 要 約

テトラヒドロフランの開環重合によりポリテトラヒドロフランを作成し、この高分子の希薄溶液において同一分子鎖の末端同士を反応させることにより環状高分子を作成した。合成した環状高分子および直鎖状高分子の分子量は約 5,000 でその分子量分布は 1.14 であった。両高分子を融体から広い温度範囲で等温結晶化させた。結晶化速度の温度依存性は両高分子とも釣鐘型の曲線を示し、明瞭な極大結晶化速度( $G_{\max}$ )が得られた。環状高分子の  $G_{\max}$  値は直鎖状高分子の  $G_{\max}$  の約 40 近くまで減少した。環状高分子の速度が遅くなる理由として多くの原因が考えられるが、主に環状分子のトポロジカルな立体構造に原因すると考えられる。また、球晶構造にも大きな違いが見出された。環状高分子は同心円状の球晶が観察されるが、直鎖状高分子は一般に観察される負の球晶が得られた。環状高分子ではトポロジカルな影響から高分子鎖の折りたたみ方向が上下のラメラ面で異なり、この違いがラメラの捩れを発現させ、球晶のパターンが同心円状になったと考えられる。

### Summary

Cyclic poly(tetrahydrofuran)s ( $M_n$  of ca. 5,000) were been prepared through the metathesis polymer cyclization of a telechelic precursor having allyl groups in the presence of a Grubbs catalyst, and the subsequent hydrogenation of the linking in the presence of an Adams' catalyst ( $PtO_2$ ). A remarkable topology effect was subsequently been observed upon the isothermal crystallization of the model polymer, showing distinctive spherulite growths rate and spherulite morphologies in comparison with the relevant linear poly(tetrahydrofuran) counterpart. The maximum growth rate of the ring polymer reduced about 40% against the linear polymer. The reduction of the growth rate in the ring polymer might be ascribed either to the conformational entropy in the molten state, to the adsorption mechanism on the crystal growth front in the secondary nucleation process, to the chain folding surface energy, or topological effect of the molecular arrangement from the melt on the crystal surface. The spherulite of the linear polymer showed a negative birefringence, as normally observed in polymer spherulites. On the contrary, the ring polymer showed a negative spherulite with a banded structure with a concentric ring.

## Introduction

Ring polymers are distinctive from their linear and branched counterparts by the absence of chain-ends (terminus) and branch points (junctions), and their unique properties often rely on this particular topology. Moreover, size-controlled ring polymers that consist exclusively of the monomer unit, in which not only chemically but also geometrically irregular, chain-end or branched structures are completely eliminated, are considered to be defect-free, and are valuable for the study of the fundamental physical chemistry and physics of randomly coiled long-chain polymers both in solution and in bulk in a more exacting manner than had been possible previously [1,2].

We have examined the isothermal crystallization of these model polymers, since a distinctive polymer topology effect is anticipated in the dynamics of the ring polymer as opposed to the linear counterpart as a result of the absence of chain ends as well as the entropic restriction of chain conformations.

## Experimental

A series of ring poly(THF)s with a 2-butenoxy linking group was synthesized through a metathesis polymer cyclization with telechelic precursors having allyl groups. The subsequent intramolecular condensation was performed under dilution at the polymer concentration of 0.2g/L ( $10^{-5}$  mol/L) in dichloromethane in the presence of a Grubbs catalyst, charged in the comparable molar quantity to allyl end groups.[3,4] The cyclized products were fully characterized by means of  $^1\text{H}$  NMR spectroscopy, matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI - TOF MS) and GPC. A relevant linear poly(THF) counterpart having ethoxy end groups was also prepared by a simple end-capping reaction of a bifunctional living poly(THF) with sodium ethoxide [2]. We used the following samples for crystallization study; ring and linear polymers with the molecular weight (GPC) of 5,100 and 5,300, respectively. Their molar disparities were 1.14 for both polymers.

The sample was melted between two cover glass plates on a Linkam LK-300 hot stage at 70°C for 5 min, then cooled down to a given crystallization temperature, and subsequently crystallized isothermally at various temperatures. The spherulite morphology and its growth rate were measured on a LK-300 temperature-controlled apparatus under a polarizing optical microscope (Olympus BH-2). Linear crystal growth rate was measured by spherulite radius as a function of time.

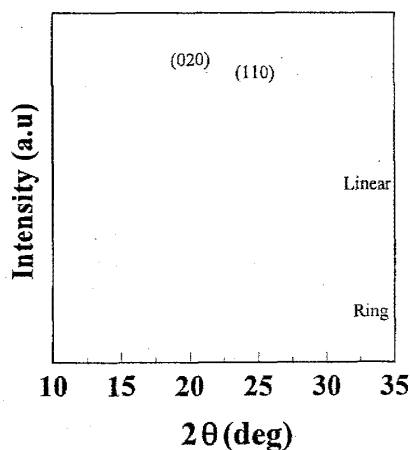


Figure 1 X-ray diffraction patterns for linear and ring polymers crystallized at 10°C.

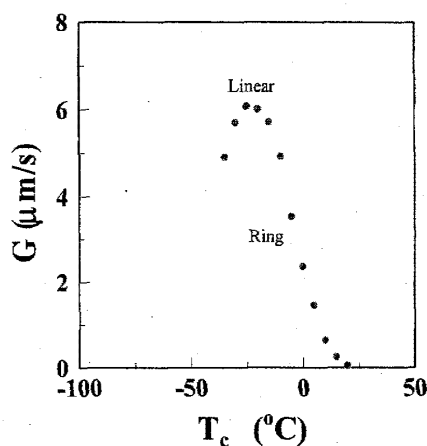


Figure 2 Temperature dependence of spherulite growth rates for linear and ring polymers.

## Results and Discussion

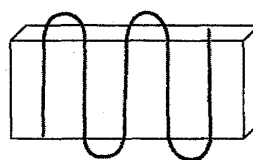
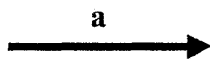
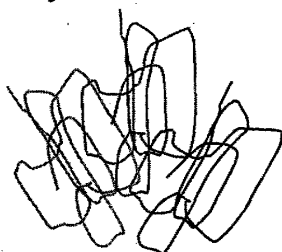
Figure-1 shows the x-ray diffraction patterns of the ring and linear polymers. Both polymers show two distinctive peaks, (020) and (110) planes, which appear at the almost the same diffraction angle. These results indicate that both polymers are constructed with the same crystal form reported by Tadokoro et al [5]. Also both polymers showed single melting peak, indicating the identical crystal structure. The equilibrium melting temperatures ( $T_m^0$ ) were determined by Hoffman-Weeks method [6]. Thus obtained equilibrium melting temperatures were 36.9°C for the ring polymer and 40.6°C for the linear polymer.

The spherulite growth rates of the linear and the ring poly(THF)s at various crystallization temperatures are shown in Figure-2. The bell-shaped curves are observed with the maximum growth rates ( $G_{\max}$ ) at  $T_{c\max}$  of -17.4°C for the ring polymer and at -24.3°C for the linear polymer. Solid lines in the figure are the results for the best fit of the experimental data based on Hoffman-Laouritzen theory [7].  $G_{\max}$  given by equation-1 is a characteristic intrinsic value in a polymer crystallization mechanism [8,9], where  $G_0$  is a constant without temperature dependence but strongly depends on the molecular weight [9,10] and the conformational entropy change during crystallization process, and  $\Delta E$  is the activation energy for the molecular transport process. The entropy contribution to  $G_0$  can be expressed as  $\exp[\Delta S/R]$ .

$$G_{\max} = G_0 \exp\left[-\frac{\Delta E}{R(2T_{c\max} - T_m^0)}\right] \quad \dots (1)$$

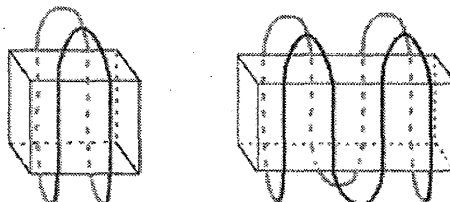
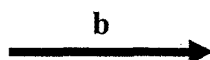
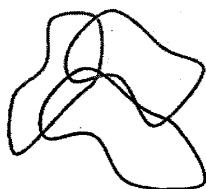
In facts, the molecular weight dependence of  $G_{\max}$  is scaled and expressed by power laws as  $G_{\max} \propto M^{-0.5}$  [9,10] for almost all crystalline polymers. The maximum growth rate of the ring poly(THF) reduces significantly against the linear counterpart (from 6.0 to 2.6  $\mu\text{m/s}$ ). The reduction of the growth

Linear Polymer



mono-layer adsorption

Ring Polymer



double-layer adsorption

Figure 3 Schematic illustration of chain folding conformation in linear (a) and ring polymer (b) crystallized from the melt.

rate in the ring polymer may be ascribed either to the conformational entropy in the molten state, to the adsorption mechanism on the crystal growth front in the secondary nucleation process, to the chain folding surface energy, or topological effect of the molecular arrangement from the melt to the crystal. In fact, the melting temperature of the ring polymer (34.5°C) is lower than that of the linear counterpart (39.6°C). Here, the enthalpy of melting in the ring polymer can be assumed to be the same with the linear polymer, since the both crystal forms are the same discussed above. This assumption yields that the entropy of fusion for the ring polymer is larger than that for the linear polymer. This indicates that the growth rate of the ring polymer will be faster than that of the linear, which is inconsistent with the experimental facts. It can be estimated the contribution of the whole exponential term in equation-1, since  $T_{cmax}$  and  $T_m$  are obtained by experimentally and  $\Delta E$  can be estimated by the best curve fitting with experimental data. Thus estimate exponential term of the ring polymer was larger than that of the linear polymer. This calculation indicates that the growth rate of the ring polymer is faster than that of linear polymer which is again inconsistent with the experimental facts. We can postulate that the topological effect in the crystallization process is the most important factor. As a practical matter, the linear polymer can be crystallized with a monolayer adsorption on the crystal growth face as shown in figure-3a. On the other hand, the ring polymer must be nucleated on the crystal growth face with the double molecular layer absorption as shown in figure-3b. These molecular arrangements are based on their topological characters. The double molecular layer nucleation requires the more nucleation energy and the crystal growth rate direction will be also changed just like a poisoning or pinning effect. These effects must reduce the growth rate for the ring polymer. However, further studies on the topology effect in the spherulite crystallization mechanism are in progress.

Figure 4 shows typical polarized optical micrographs of spherulites crystallized at 10°C for linear (a) and ring (b) poly(THF)s. The former spherulite shows a negative birefringence, as normally observed in polymer spherulites. On the contrary, the latter shows a negative spherulite with a banded structure with a concentric ring pitch of about 7  $\mu\text{m}$ . The banded spherulites indicate rotation of the optical indicatrix along a radial direction. This rotation is caused by the lamellae twisting, which is associated

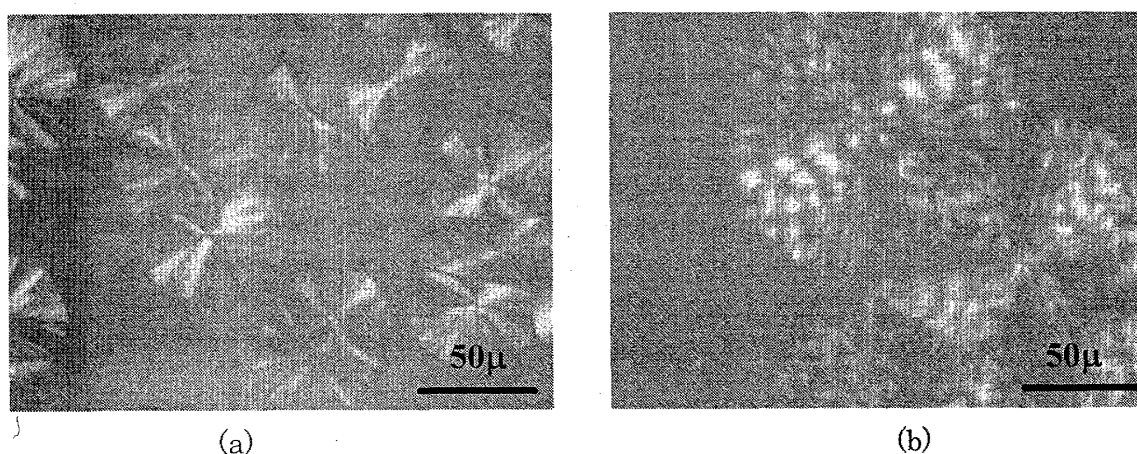


Figure 4 Optical photographs under polarizing optical microscope. Samples (a: linear and b: ring polymers) were crystallized at 10°C from the melt.

with cumulative reorientation of lamella at successive screw dislocation [11,12] or different surface stresses on opposite fold surfaces of individual lamella [13,14]. The surface stress tends to be developed by the fold structures, such as uneven fold volume, and the morphological difference observed between the linear and the ring poly(THF)s might be caused by the distinctive chain folding structures. As seen in figure-3b, the chain folding surface in the ring polymer will built up with two different chain folding directions, yielding the different surface energy between the up and down lamellar surface. This surface difference gives rise to the lamellar twisting, appearing banded spherulite. On the other hand, the fold surface in the linear polymer can be constructed with the same chain folding manner on both up and down lamella surfaces as seen in figure-3a.

## Conclusions

The ring polymer exhibited the lower equilibrium melting temperature and slower the spherulite growth rate than the corresponding linear polymer. The polymer showed the banded spherulite while the linear polymer showed the commonly observed negative spherulite. These characteristics in the ring polymer can be associated with the topological effect in the crystallization process.

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